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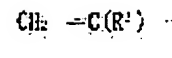
(54) RARE EARTH ELEMENT-CONTAINING RESIN AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a rare earth element-containing resin having excellent selective absorption characteristics of radiation and electromagnetic radiation by polymerizing a resin-forming raw material comprising a methacrylic acid ester as a main component, a salt of a rare earth element and an unsaturated fatty acid, a solvent and a polymerization initiator in a mold.

I



II

III

CONSTITUTION: A mixture consisting of (A) a monomer comprising methacrylic acid ester as a main component and/or its partial polymer, (B) a salt (e.g. lanthanum) of B1: a rare earth element selected from lanthanum, cerium, praseodymium, dysprosium, thulium, yttrium and lutetium and B2: an unsaturated fatty acid selected from formula I and formula II [R1 is H or 1-3C hydrocarbon group; R2 is 2-6C alkylene group; R3 is 2-6C (un)saturated hydrocarbon group], (C) a solvent (e.g. methacrylic acid) of formula III [R1 is 11-20C (un)saturated hydrocarbon group] showing solubility of the components A and B and (D) a polymerization initiator is polymerized in a mold to give the objective resin containing 0.001-35wt.% rare earth element.

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CLAIMS

[Claim 1] the radiation and electromagnetism which are characterized by providing the following -- the rare-earth element content resin excellent in the selective-absorption nature of a line (a) The monomeric unit which makes a methacrylic ester a principal component. (b) A lanthanum, a cerium, a praseodymium, a dysprosium, a thulium, The rare-earth element chosen from the group which consists of an ytterbium and a lutetium, and general formula CH2 =C(R1)-COOH (among a formula) R1 is general formula CH2 =C (R1)-CO2-R2-OCO-R3-COOH (among a formula), and it is hydrogen or the hydrocarbon residue of carbon numbers 1-3. R1 It is hydrogen or the hydrocarbon residue of carbon numbers 1-3, and is R2. It is the alkylene machine of carbon numbers 2-6, and is R3. At least a kind of monomeric unit chosen from the group which consists of a salt with the unsaturated fatty acid chosen from the group which consists of being the saturation or the unsaturated-hydrocarbon residue of carbon numbers 2-6.

[Claim 2] The rare-earth element content resin according to claim 1 whose amount of a rare-earth element is 0.001 - 35 % of the weight as a rare-earth element on the weight criteria of a resin.

[Claim 3] (a) The resin formation raw material chosen from the group which consists of monomers which contain a methacrylic ester as a principal component, and those partial polymers, (b) A lanthanum, a cerium, a praseodymium, a dysprosium, a thulium, The rare-earth element chosen from the group which consists of an ytterbium and a lutetium, and general formula CH2 =C(R1)-COOH (among a formula) R1 is general formula CH2 =C (R1)-CO2-R2-OCO-R3-COOH (among a formula), and it is hydrogen or the hydrocarbon residue of carbon numbers 1-3. R1 It is hydrogen or the hydrocarbon residue of carbon numbers 1-3, and is R2. It is the alkylene machine of carbon numbers 2-6. R3 it was chosen out of the group which consists of a salt with the unsaturated fatty acid chosen from the group which consists of being the saturation or the unsaturated-hydrocarbon residue of carbon numbers 2-6 -- at least -- a kind -- (c) The above-mentioned component (a) And (b) General formula R1-COOH(inside of formula and R1 are hydrocarbon residues of saturation [of carbon numbers 1-20], or unsaturation); which receives and shows solubility.

R2-OCO-R3-COOH(R2 is hydrogen or hydrocarbon residue of carbon numbers 1-9 among formula, and R3 is hydrocarbon residue of saturation [of carbon numbers 1-4], or unsaturation);.

CH2 =C(R4)-COO-(-A1-O-) nH(R4 is hydrogen or methyl group among formula, A1 is alkylene machine of carbon numbers 2-6, and n is integer of 0, or 1-10);.

CH2 =C(R5)-COO-R6-OH(R5 is hydrogen or methyl group among formula, and R6 is alkylene machine of carbon numbers 2-6);.

R7-OH(inside of formula and R7 are hydrocarbon residues of saturation [of carbon numbers 3-10], or unsaturation);, and R8=(-A2-O-) mH (among a formula) R8 It is the hydrocarbon residue of the saturation of a hydroxyl group or carbon numbers 1-10, or an unsaturation. A2 At least one sort of solvents chosen from the group which consists of a compound of it being the alkylene machine of carbon numbers 2-4, and m being the integer of 1-10, and (d) the radiation characterized by carrying out the polymerization of the mixture which consists of a polymerization initiator in mold, and electromagnetism -- manufacturing method of the rare-earth element content resin excellent in the selective-absorption nature of a line

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the rare-earth element content resin which has many physical properties, such as radiation originating in a rare-earth element and the selective-absorption nature of an electromagnetic wave, and a luminescence, in more detail, and its manufacturing method about the resin containing the rare-earth element chosen from the group which consists of a lanthanum, a cerium, a praseodymium, a dysprosium, a thulium, an ytterbium, and a lutetium.
[0002]
[Description of the Prior Art] Conventionally, as an additive to the synthetic resin which absorbs the light of the specific wavelength of a visible region alternatively, many oil colors, such as an azo system, diazo **, and an ANSURA quinone system, are known. Although these have the advantage in which it can be used making it able to dissolve in a resin raw material, if the wavelength dependency of absorption is seen, they will be absorbed over the large wavelength range. Namely, it becomes broadcloth absorption, and since it will be absorbed from the wavelength of 350nm to the beam of light of the large range of 500nm if you are going to make it fully absorb the beam of light near the wavelength of 450nm for this reason, depending on the use of selective absorption, it becomes a fault. Moreover, generally weatherability is inferior in these colors, and, in a certain case, there are many irradiation of the sunlight for about one week or things to which absorption becomes weaker or disappears at the temperature of about 180 degrees C.
[0003] It is known that will add a lead compound, a bismuth compound, etc. to synthetic resin, and transparent synthetic resin will be obtained in a visible region on the other hand in absorption of the X-ray and gamma ray which are the electromagnetic wave of short wavelength further rather than a visible ray. If a mass absorption coefficient (cm2 / g) is seen as a numeric value which shows the absorptance of a photon, since the absorption end energy accompanying the changes between orbits of an atomic orbital electron changes with atoms, in the energy field of an X-ray and a gamma ray, the value of a mass absorption coefficient will change discontinuously. That is, when the mass absorption coefficient of lead and a cerium is compared, it is L3 of a cerium. It is L3 of lead from the absorption end (5.723keV). Between the leaden L3-K absorption end (74.960keV), it is known from K absorption end (40.440keV) of between the absorption end (13.040keV) and a cerium that the direction of a cerium has a mass absorption coefficient several times as large as lead.
[0004] It is the same similarly about the element from the thallium of the atomic number 81 to the palladium of the atomic number 46. Therefore, if the energy range of a photon is limited and considered, it will be understood that there is respectively characteristic bigger photon absorption ability than lead in various kinds of elements.
[0005]
[Problem(s) to be Solved by the Invention] General organic synthetic resin found out the resin which this invention person uses that sharp specific absorption peculiar to each is shown if this is made to contain a rare-earth element, although absorption usually is not

seen to the electromagnetic wave of a near-infrared beam of light, a visible ray, an ultraviolet beam of light and an X-ray, and a gamma ray field, and there is weatherability which is not seen by the former, and has the selective-absorption performance of an electromagnetic wave.

[0006]

[Means for Solving the Problem] The rare-earth element content resin of this invention is (a). The monomeric unit which makes a methacrylic ester a principal component, (b) A lanthanum, a cerium, a praseodymium, a dysprosium, a thulium, The rare-earth element chosen from the group which consists of an ytterbium and a lutetium, and general formula CH2 =C(R1)-COOH (among a formula) R1 is general formula CH2 =C (R1)-CO2-R2-OCO-R3-COOH (among a formula), and it is hydrogen or the hydrocarbon residue of carbon numbers 1-3. R1 It is hydrogen or the hydrocarbon residue of carbon numbers 1-3, and is R2. It is the alkylene machine of carbon numbers 2-6. R3 what contains at least a kind of monomeric unit chosen from the group which consists of a salt with the unsaturated fatty acid chosen from the group which consists of being the saturation or the unsaturated-hydrocarbon residue of carbon numbers 2-6 -- it is -- radiation and electromagnetism -- it excels in the selective-absorption nature of a line

[0007] The amount of the rare-earth element used for the resin of this invention is 0.001% or 35% as a rare-earth element on the weight criteria of a resin, and since it will spoil the mechanical physical properties of a resin constituent if the effect which originates in a rare-earth element if fewer than 0.001% is small and exceeds 35%, it is not desirable.

[0008] These rare-earths element can make a rare-earth element contain in a resin by carrying out copolymerization of a kind to the monomers which were chosen from the group which consists of a salt with these specific unsaturated fatty acid of a **** element and the above and which contain a methacrylic ester as a principal component, or those partial polymers at least. It is (a) in order to obtain the transparent resin which does not have dispersion especially. The resin formation raw material chosen from the group which consists of monomers which contain a methacrylic ester as a principal component, and those partial polymers, (b) A lanthanum, a cerium, a praseodymium, a dysprosium, a thulium, The rare-earth element chosen from the group which consists of an ytterbium and a lutetium, and general formula CH2 =C(R1)-COOH (among a formula) R1 is general formula CH2 =C (R1)-CO2-R2-OCO-R3-COOH (among a formula), and it is hydrogen or the hydrocarbon residue of carbon numbers 1-3. R1 It is hydrogen or the hydrocarbon residue of carbon numbers 1-3, and is R2. It is the alkylene machine of carbon numbers 2-6. R3 it was chosen out of the group which consists of a salt with the unsaturated fatty acid chosen from the group which consists of being the saturation or the unsaturated-hydrocarbon residue of carbon numbers 2-6 -- at least -- a kind -- (c) The above-mentioned component (a) And (b) General formula R1-COOH(inside of formula and R1 are hydrocarbon residues of saturation [of carbon numbers 1-20], or unsaturation); which receives and shows solubility.

R2-OCO-R3-COOH(R2 is hydrogen or hydrocarbon residue of carbon numbers 1-9 among formula, and R3 is hydrocarbon residue of saturation [of carbon numbers 1-4], or unsaturation);.

CH2 =C(R4)-COO-(-A1-O-) nH(R4 is hydrogen or methyl group among formula, A1 is alkylene machine of carbon numbers 2-6, and n is integer of 0, or 1-10);.

CH2 =C(R5)-COO-R6-OH(R5 is hydrogen or methyl group among formula, and R6 is alkylene machine of carbon numbers 2-6);.
R7-OH(inside of formula and R7 are hydrocarbon residues of saturation [of carbon numbers 3-10], or unsaturation);, and R8=(-A2-O-) mH (among a formula) R8 It is the hydrocarbon residue of the saturation of a hydroxyl group or carbon numbers 1-10, or an unsaturation. A2 They are at least one sort of solvents which are the alkylene machines of carbon numbers 2-4, and were chosen from the group which consists of a compound of m being the integer of 1-10, and (d). The manufacturing method of the rare-earth element content resin which consists of carrying out the polymerization of the mixture which consists of a polymerization initiator in mold is suitable.
[0009] As a methacrylic ester, alkyl methacrylate, such as a methyl methacrylate and an ethyl methacrylate, Or cyclohexyl methacrylate, a methacrylic-acid tetrahydro furil, A methacrylic-acid benzyl, a methacrylic-acid phenyl, a methacrylic-acid allyl compound, Methacrylic-acid metallyl, a methacrylic-acid beta-naphthyl, methacrylic-acid beta-aminoethyl, Methacrylic-acid 2-methoxy ethyl, ethylene glycol dimethacrylate, Diethylene-glycol dimethacrylate, tetraethylene-glycol dimethacrylate, Polyethylene glycol dimethacrylate, 1, 4-butanediol dimethacrylate, They are 1, 6-hexanedioldimethacrylate, a neopentyl glycol JIMETA chestnut coat, pentaerythritol tetrapod methacrylate, trimethylolpropanetrimethacrylate, these halogenation methacrylate, etc.
[0010] The aforementioned general formula (1) (2) (3) (4) (5) It reaches. The solvent shown by (6) It is a cosolvent for dissolving a rare-earth element compound in a resin formation raw material uniformly. Specifically For example, unsaturated carboxylic acids, such as a methacrylic acid and an acrylic acid, A propionic acid, an isobutyric acid, n-butanoic acid, a caproic acid, a caprylic acid, a capric acid, The fatty acid of saturation, such as 2-ethyl hexanoic acid, stearin acid, and a naphthenic acid, or an unsaturation, Unsaturated alcohols, such as alpha-hydroxyethyl acrylate and alpha-hydroxyethyl methacrylate, Polyhydric alcohol, such as saturated-fat group alcohol, such as propyl alcohol and cyclohexyl alcohol, ethylene glycol, a diethylene glycol, and a propylene glycol, is raised.
[0011] The monomer which has a methyl methacrylate and copolymerization nature like a methacrylic acid, an acrylic acid, alpha-hydroxyethyl methacrylate, alpha-hydroxyethyl acrylate, etc. is desirable among these solvents. These solvents are independent or can be used combining two or more sorts. Although the amount of the above-mentioned solvent used cannot generally be decided with the kind of rare-earth element compound to be used, and an amount, it is 10 or less % of the weight preferably 40 or less % of the weight. Since mechanical and the thermal property of a resin constituent which are obtained are reduced when the amount used exceeds 40 % of the weight, it is not desirable.
[0012] As a polymerization initiator used in the above-mentioned copolymerization, a well-known radical initiator like azobis systems, such as - azobis (2,4-dimethylvaleronitrile), and peroxide system [, such as benzoyl peroxide and lauroyl peroxide,], alpha, and alpha'-azobisisobutyronitril, alpha, and alpha'alpha, alpha'-azobis (2, 4-dimethyl-4-methoxy valeronitrile), can be used, for example. Being able to mix and use that these polymerization initiators are independent or two sorts or more, the amount used is 0.001 or the 0.1 weight section to the resin raw material 100 weight section.

[0013] Although not limited especially as a copolymerization method for obtaining the resin of this invention, a cast polymerization is raised as a desirable copolymerization method. the case of this cast polymerization -- the aforementioned component (a) and (b) (c) and -- The mixture prepared from (d) is poured in into the mold which consisted of a cell which consists of for example, inorganic glass, a stainless steel, nickel chromium, or aluminum, and a gasket, and carries out a polymerization. Radiation polymerization can also be made to perform with the degree of low temperature below a room temperature in the case of a special use. Usually, there is no 0.3 at 45 or 95 degrees C, 15-hour 10 minutes cannot be found at 100 or 145 degrees C further succeedingly, and a polymerization is completed over 5 hours.

[0014] The optical-absorption agent for making the light of the wavelength of an ultraviolet ray absorbent, a release agent, a thermostabilizer, and others absorb if needed in this invention, an optical dispersing agent, a radiation shielding material, etc. can also be added.

[0015] Although the rare-earth element content resin of this invention which consists of composition which was described above can make the refractive index of a base-material resin other than the optical selective-absorption performance resulting from a rare-earth element able to increase, or can give the absorptance of radiation to an X-ray and a gamma ray, and the absorptance to a thermal neutron line and can use them for a filter, a lens, lighting covering, the screen for images, the protection filter to radiation, a scintillator, an emitter, etc., it is not limited to these.

[0016] Next, this invention is not limited although an example explains this invention in more detail.

Example 1 methacrylic-acid lanthanum 8g, 2g [of n-octylic acid], and propylene-glycol 1g, alpha-hydroxyethyl methacrylate 1g, styrene 5g, and 83g of methyl methacrylates were mixed. This mixed liquor was transparent and colorless liquid.

[0017] Next, after adding 0.005g dioctyl sulfosuccinate sodium salt into this mixed liquor as 0.04g alpha and alpha'-azobis (2,4-dimethylvaleronitrile) and a release agent as a polymerization catalyst and making it dissolve in it, Deaerated and poured in into the mold of the inorganic glass of the conventional method set up so that the board thickness of a product might be beforehand set to 2mm, and it was immersed into 65-degree C warm water for 180 minutes, subsequently to under a 110-degree C air bath this mold was made to stay for 120 minutes, and the polymerization was completed. The resin board picked out from mold was transparent and colorless.

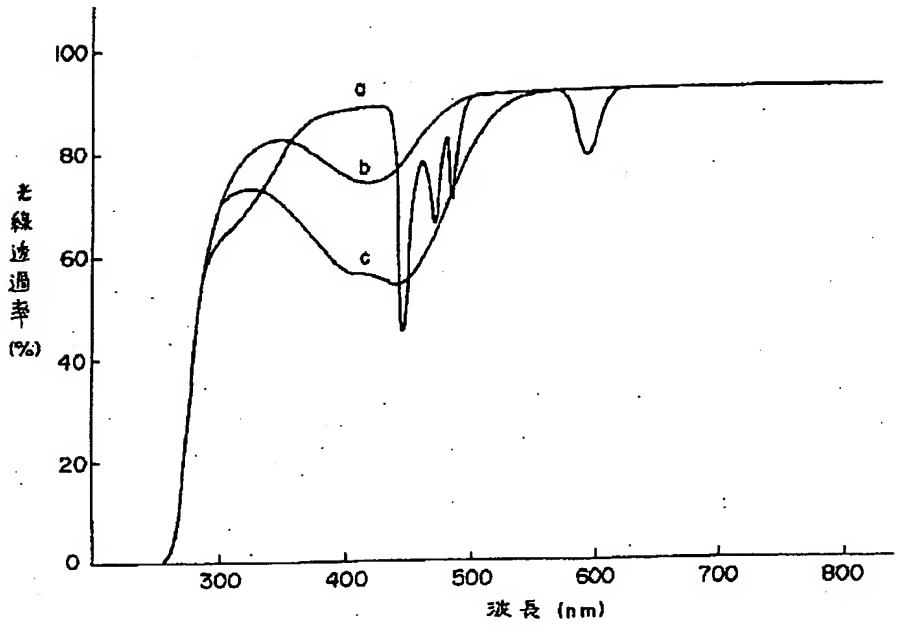
Example 2 methacrylic-acid neodymium 4g, methacrylic-acid lanthanum 4g, 4g [of lauric acids], and propylene-glycol 1g was mixed and dissolved in 87g of methyl methacrylates, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was pink transparence.

Example 3 methacrylic-acid praseodymium 8g, 2g [of n-octylic acid], and propylene-glycol 1g, alpha-hydroxyethyl methacrylate 1g, styrene 5g, and 83g of methyl methacrylates were mixed, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was a transparent board of light yellowish green.

Example 4 methacrylic-acid neodymium 4g, methacrylic-acid praseodymium 4g, 4g [of lauric acids], and propylene-glycol 1g was mixed and dissolved in 87g of methyl methacrylates, and the cast polymerization was performed on the same polymerization

conditions as an example 1. The obtained resin board was transparent and was carrying out light yellowish green.
Example 5 methacrylic-acid praseodymium 20g, 7g [of lauric acids], and propylene-glycol 4g and 69g of methyl methacrylates were mixed, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was transparent at yellowish green.
Example 6 methacrylic-acid praseodymium 20g, 7g of lauric acids, and 73g of methyl methacrylates were mixed, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was transparent at yellowish green.
Example 7 methacrylic-acid praseodymium 20g, 7g [of lauric acids], and tetrahydro furil methacrylate 73g was mixed, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was transparent at yellowish green.
Example 8 methacrylic-acid thulium 8g, 2g [of n-octylic acid], and propylene-glycol 1g, alpha-hydroxyethyl methacrylate 1g, styrene 5g, and 83g of methyl methacrylates were mixed, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was a pale red transparent board.
Example 9 methacrylic-acid neodymium 4g, methacrylic-acid dysprosium 4g, 4g [of lauric acids], and propylene-glycol 1g was mixed and dissolved in 87g of methyl methacrylates, and the cast polymerization was performed on the same polymerization conditions as an example 1. The obtained resin board was transparent and was carrying out light yellow.
Example SUPIRON yellow GRCH-Specialof comparison (Hodogaya chemistry company product) 0.002g and flax plus flume yellow AGB(American aniline company product)0.005g were dissolved in 100g of methyl methacrylates, respectively, and the cast polymerization was performed on the same polymerization conditions as an example 1, respectively. The obtained resin board was transparent in light yellow respectively.
The example shows broadcloth absorption that each resin board obtained in the example and the example of comparison is known with the spectral transmittance curve of a view 1 although absorption is seen near the wavelength of 450nm for sharp absorption in the example of comparison. Moreover, although the intensity of absorption did not change these in the example when the outdoor exposure was carried out for summer one month in Otake-shi, Hiroshima, the color has almost disappeared in the example of comparison.
[0018]
[Effect of the Invention] The rare-earth element content resin of this invention has many physical properties, such as radiation originating in a rare-earth element and the selective-absorption nature of an electromagnetic wave, and a luminescence, and has weatherability, and makes the refractive index of a base-material resin increase, and can be used for a filter, a lens, lighting covering, the screen for images, the protection filter to radiation, a scintillator, an emitter, etc.

[Translation done.]


100
80
60
40
20
0
光線透過率 (%)
a
b
c
300
400
500
600
700
800
波長 (nm)